Oxozirconium Methacrylate Clusters: $Zr_6(OH)_4O_4(OMc)_{12}$ and $Zr_4O_2(OMc)_{12}$ (OMc = Methacrylate)

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The crystalline oxozirconium methacrylate clusters $Zr_6(OH)_4O_4(OMc)_{12}$ and $Zr_4O_2(OMc)_{12}$ were obtained by reaction of $Zr(OnPr)_4$ with an excess of methacrylic acid and analysed by X-ray diffraction. The oxide and hydroxide groups are in a μ_3-bridging mode in both structures, and the methacrylate ligands are chelating or bridging. The zirconium atoms in $Zr_6(OH)_4O_4(OMc)_{12}$ form an octahedron, the cluster having crystallographic C_{3v} symmetry. Each metal atom is square-antiprismatically coordinated by eight oxygen atoms. In $Zr_4O_2(OMc)_{12}$, the zirconium atoms have a distorted butterfly arrangement; their coordination geometry is square-antiprismatic or capped octahedral.

The high reactivity of metal alkoxides, $E(OR)_n$, towards water often necessitates the use of chemical additives (mostly bidentate ligands L, such as acetate or acetylacetonate) to moderate their reactivity in sol-gel processes. By substitution of some of the alkoxide groups, a new molecular precursor, $E(OR)_{n-x}L_x$, is formed which exhibits a different reactivity. Upon addition of water, the E−OR groups are primarily hydrolyzed[1]. The bidentate ligands inevitably lower the degree of cross-linking in the thus obtained oxide materials $EO_{(n-x)/2}L_x$, because they block condensation sites. Deliberate adjustment of the $E(OR)_n/L$ ratio therefore also allows control of the size of the primary building blocks (i.e., the primarily obtained oxo clusters) and thus the architecture of the final materials[2].

The potential for synthesizing novel materials originating from the presence of organic groups in the modifying ligands L was hardly realized until recently. Organo*functional* ligands L not only block condensation sites like their non-functional counterparts, but additionally introduce chemical functions. They allow extensive chemical modifications of the whole system and the development of materials with new properties[3,4].

The most obvious choices for L are functionalized carboxylates, because they are readily available. Reaction of carboxylic acids with metal alkoxides provides derivatives $E(OR)_{n-x}[OOC{-}X{-}A]_x$ where the functional group A is linked via the carboxylate group and some spacer X to the metal alkoxide moiety.

In the reaction of $Ti(OR)_4$ with carboxylic acids, the maximum degree of substitution achieved to date is 1.33. An excess of carboxylic acid results in partial hydrolysis, due to the in situ production of water by the esterification of the carboxylic acid with the cleaved alcohol. The crystalline clusters $Ti_6O_4(OR)_8(OOC{-}R')_8$ (R' = Me: R = Et, *n*Bu, *i*Pr[5]; R' = C(Me)=CH$_2$: R = Et[6]), $Ti_6O_4(OR)_{12}(OOC{-}R')_4$ (R' = Me: R = *i*Pr[7]; R' = μ_3-$CCo_3(CO)_9$: R = Et[8] – different linkage of the coordination octahedra) and $Ti_4O_4(OR)_4[OOC{-}CCo_3(CO)_9]_4$ (R = *i*Pr, Ph)[8] have been thus obtained as primary hydrolysis products. The titanium atoms in each of these clusters are octahedrally coordinated by oxygen atoms, and the carboxylate groups are exclusively in a bridging mode. The organic groups are at the periphery of the cluster; the functional groups, as in the methacrylate derivative [R' = C(Me)=CH$_2$], are therefore fully accessible for further reactions.

The structural information from these clusters allows conclusions to be made on how the building blocks in the (amorphous!) gels, obtained after complete hydrolysis of the organically modified alkoxide precursors, are composed and interconnected.

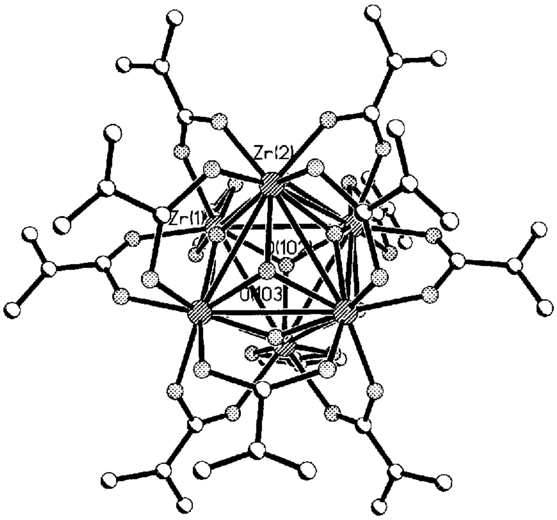
In contrast to the reactions of $Ti(OR)_4$ with carboxylic acids, no corresponding crystalline derivative has hitherto been obtained from $Zr(OR)_4$. A different structural chemistry was expected, because of the preference of Zr for coordination numbers higher than 6. Furthermore, earlier experiments had already shown that more than 1.33 OR groups per metal atom can be substituted when methacrylic acid is treated with $Zr(OR)_4$ instead of $Ti(OR)_4$[6]. In this paper we report the structure of two crystalline oxozirconium methacrylate clusters obtained by reaction of $Zr(OnPr)_4$ with methacrylic acid (McOH).

Results

Two crystalline compounds were obtained when a 70% solution of $Zr(OnPr)_4$ in propanol was treated with an excess of methacrylic acid, their constitution depending on the molar ratio of the reactants. Cluster **1** crystallized quantitatively after one day when a 4-fold molar excess was employed, while cluster **2** was obtained quantitatively after 7 days with a 15-fold excess.

In cluster **1** (Figure 1), the Zr atoms have an octahedral arrangement [Zr−Zr 348.0(2) and 354.8(4) pm]. It has a crystallographic C_{3v} symmetry with the C_3 axis passing through the center of two opposite triangular faces of the octahedron and the mirror planes bisecting these faces. The cluster contains 12 methacrylate ligands. Three of them chelate the three symmetry-equivalent Zr(1) atoms, while the other nine OMc groups bridge the Zr(1)−Zr(2) and Zr(2)−Zr(2)′ edges. Thus, the eight triangular faces of the Zr_6 octahedron are edge-bridged in different ways: Each of the edges of the Zr(2), Zr(2)′, Zr(2)″ triangle and the three symmetry-equivalent Zr(2), Zr(2)′, Zr(1) triangles are bridged by OMc groups, while there are only two bridged edges in the three Zr(1), Zr(1)′, Zr(2) triangles and none in the Zr(1), Zr(1)′, Zr(1)″ triangle (Figure 2).

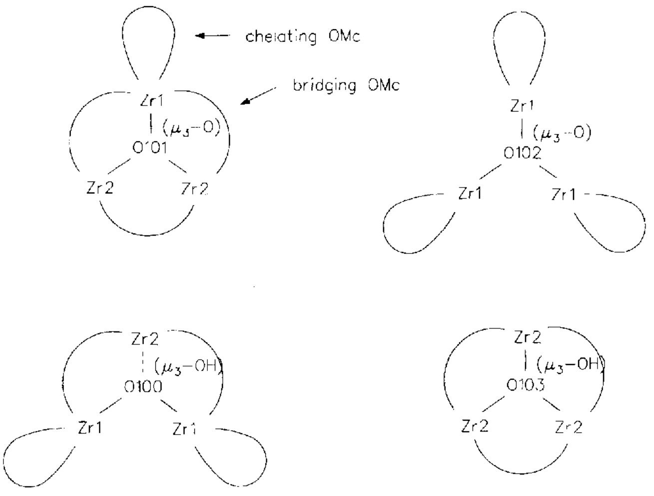
Figure 1. The structure of the cluster $Zr_6(OH)_4O_4(OMc)_{12}$ (**1**)[a]



[a] Selected bond lengths [pm] and angles [°]: Zr(1)−Zr(2) 348.0(2), Zr(1)−Zr(1)′ 350.6(4), Zr(2)−Zr(2)′ 354.8(4), Zr(1)−O(100) 217(1), Zr(1)−O(101) 206(1), Zr(1)−O(102) 209.5(5), Zr(1)−O(200) 219(2), Zr(1)−O(300) 233(2), Zr(2)−O(100) 241(2), Zr(2)−O(101) 205.0(7), Zr(2)−O(103) 229(1), Zr(2)−O(201) 213(2), Zr(2)−O(210) 210(2); Zr(1)−O(100)−Zr(1)′ 107.6(7), Zr(1)−O(100)−Zr(2) 98.6(5), Zr(1)−O(101)−Zr(2) 115.5(4), Zr(2)−O(101)−Zr(2)′ 119.8(7), Zr(1)−O(102)−Zr(1)′ 113.7(4), Zr(2)−O(103)−Zr(2)′ 101.4(7), O(100)−Zr(1)−O(101) 75.1(5), O(100)−Zr(1)−O(102) 69.1(4), O(101)−Zr(1)−O(102) 95.5(7), O(100)−Zr(2)−O(101) 70.2(5), O(100)−Zr(1)−O(103) 120.9(7), O(101)−Zr(1)−O(103) 69.3(5).

Each of the Zr_3 triangles in the Zr_6 octahedron is capped by either a μ_3-O or a μ_3-OH group. The hydrogen atoms could not be located, but charge balancing requires the presence of four OH groups. Thus, the cluster must have the composition $Zr_6(OH)_4O_4(OMc)_{12}$. As mentioned in the introduction, the source of the oxide and hydroxide ions is water generated by esterification of methacrylic acid with propanol. The crystallographic 3-fold axis passes through two oxygen atoms [O(102) and O(103)], one of which is a μ_3-O and the other belongs to a μ_3-OH group. Based on the Zr−O bond lengths, O(102) should be the bridging oxygen atom [Zr(1)−O(102) 209.5(5) pm] and O(103) the bridging OH group [Zr(2)−O(103) 229(1) pm]. There are two oxygen atoms in general positions [O(100) and O(101)] bridging the remaining six faces of the octahedron (each repeated three-times by symmetry). The oxygen atom O(101) is clearly a μ_3-O group; it is symmetrically located above the Zr(1), Zr(2), Zr(2)′ faces [Zr(1)−O(101) 206(1) pm, Zr(2)−O(101) 205.0(7) pm]. In contrast, O(100) is asymmetrically bonded, with two short bonds [217(1) pm] to the Zr(1) atoms, and a very long bond to Zr(2) [241(2) pm].

Figure 2. The different types of O- or OH-capped Zr triangles in $Zr_6(OH)_4O_4(OMc)_{12}$ (**1**)

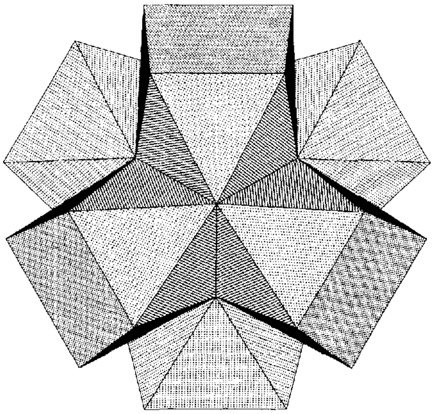


Thus, O(100) is clearly a bridging OH group being closer to a μ_2 than to a μ_3 bonding situation. This asymmetric bonding of the OH group may be caused by the chelating OMc groups at Zr(1). The weaker Zr−O bonds of the chelating group [Zr(1)−O(300) 233(2) pm, compared to Zr−O of 210−219 pm for the bridging OMc groups] are probably compensated by stronger bonds of Zr(1) to the bridging OH group. The different types of O- or OH-capped Zr triangles in $Zr_6(OH)_4O_4(OMc)_{12}$ are schematically shown in Figure 2. The Zr_6O_8 core of this cluster closely resembles the U_6O_8 core in $U_8(O/OH)_8(Ph_2PO_4)_{12}$, reported recently[9]. Only bridging diphenylphosphate ligands were observed in this structure.

Each of the Zr atoms is square-antiprismatically coordinated by eight oxygen atoms. One square face is formed by the oxygen atoms of the (chelating or bridging) OMc ligands. The opposite square face is formed by two μ_3 oxide and two μ_3 hydroxide groups. Each square antiprism therefore shares an edge with the four neighbouring ZrO_8 antiprisms (Figure 3).

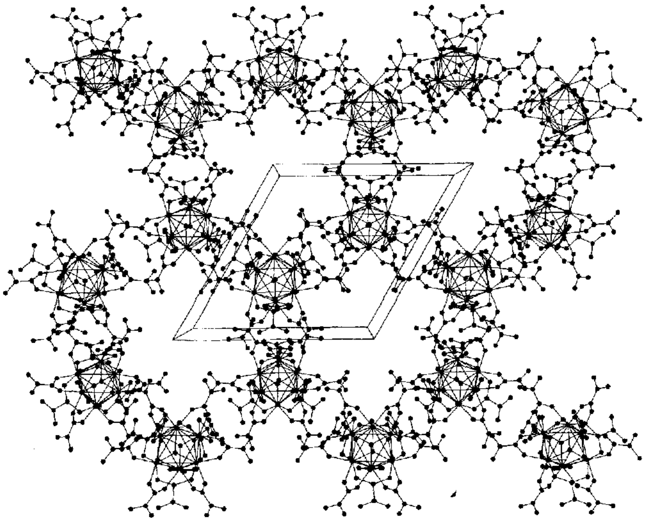
The packing diagram (Figure 4) shows that the crystal lattice has rather large voids parallel to the *c*-axis. This is also reflected in the low density of the compound. In these channels we found the highest residual electron density after refinement of the structure. Although this strongly indicates the presence of organic molecules there, they must be highly disordered, because we were unable to locate any groups. Owing to these missing groups and to some oscillation of the clusters about the 3-fold axis (as indicated by

Figure 3. The linking of the coordination polyhedra in $Zr_6(OH)_4O_4(OMc)_{12}$ (**1**)



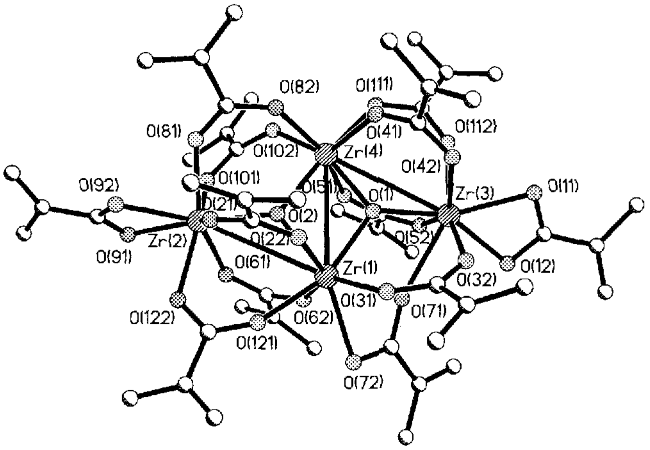
increasing B-values from the center to the periphery of the clusters), the R-value for the structure is rather high.

Figure 4. Packing of the $Zr_6(OH)_4O_4(OMc)_{12}$ (**1**) clusters



Cluster **2** has the composition $Zr_4O_2(OMc)_{12}$ (Figure 5). The four zirconium atoms have a distorted butterfly arrangement, the dihedral angle between the Zr(1), Zr(3), Zr(4) and Zr(1), Zr(2), Zr(4) planes being 9.66°. The Zr_3 triangles are capped by a μ_3-oxygen atom from different sides. Although all Zr−Zr edges [except the intraannular Zr(1)−Zr(4)] are bridged by OMc ligands, their distances are distinctly longer than in **1**, Zr(3)−Zr(4) [358.92(6) pm] being the shortest, and Zr(2)−Zr(4) the longest (374.5 pm).

Figure 5. The structur of the cluster $Zr_4O_2(OMc)_{12}$ (**2**)[a]



[a] Selected bond lengths [pm] and angles [°]: Zr(1)−Zr(2) 367.73(6), Zr(1)−Zr(3) 360.22(6), Zr(1)−Zr(4) 335.32(6), Zr(2)−Zr(4) 374.5(6), Zr(3)−Zr(4) 358.92(6), Zr(1)−O(1) 207.4(3), Zr(1)−O(2) 217.3(3), Zr(1)−O(22) 217.4(3), Zr(1)−O(31) 220.6(3), Zr(1)−O(62) 214.1(3), Zr(1)−O(71) 233.0(3), Zr(1)−O(72) 230.6(3), Zr(1)−O(121) 215.5(3), Zr(2)−O(2) 203.0(3), Zr(2)−O(21) 223.8(3), Zr(2)−O(61) 224.1(3), Zr(2)−O(91) 226.0(3), Zr(2)−O(92) 229.4(3), Zr(2)−O(81) 218.7(3), Zr(2)−O(101) 218.7(3), Zr(2)−O(122) 218.9(3), Zr(3)−O(1) 202.8(3), Zr(3)−O(11) 227.1(3), Zr(3)−O(12) 220.1(3), Zr(3)−O(32) 213.5(3), Zr(2)−O(42) 219.7(3), Zr(3)−O(52) 215.6(3), Zr(3)−O(112) 217.6(3), Zr(3)−O(71) 248.8(3), Zr(4)−O(1) 204.4(3), Zr(4)−O(2) 205.7(3), Zr(4)−O(41) 219.4(3), Zr(4)−O(51) 224.8(3), Zr(4)−O(82) 219.9(3), Zr(4)−O(102) 215.6(3), Zr(4)−O(111) 218.9(3); Zr(1)−O(1)−Zr(3) 122.9(1), Zr(1)−O(1)−Zr(4) 109.1(1), Zr(3)−O(1)−Zr(4) 123.6(1), Zr(1)−O(2)−Zr(2) 122.0(1), Zr(1)−O(2)−Zr(4) 109.0(1), Zr(2)−O(2)−Zr(4) 132.8(2).

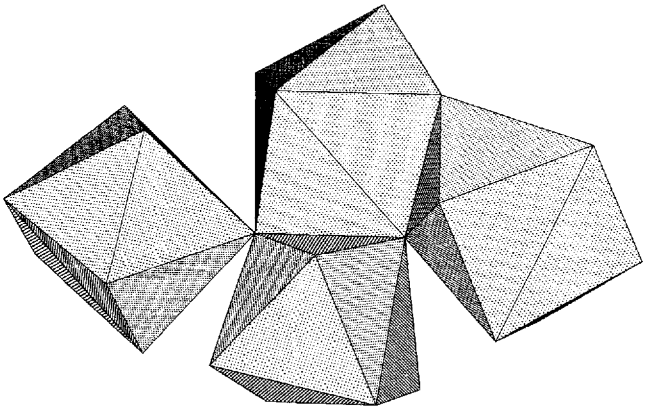
The most prominent feature of the structure of **2** is its asymmetry. Three of the four Zr atoms are square-antiprismatically coordinated by eight oxygen atoms, but with different coordination environments. The fourth Zr atom [Zr(4)] is only 7-coordinate (distorted capped octahedron). There are three different coordination modes of the OMc ligands: two are chelating [at Zr(2) and Zr(3)], nine are symmetrically bridging (with one to three bridges per Zr−Zr edge), and one is in the rare η^2,μ_2-coordination mode in which one of the oxygen atoms of a chelating carboxylate group [O(71)] additionally coordinates to another metal atom.

While one of the μ_3-oxygen atoms [O(1)] is located quite symmetrically above the Zr_3 triangle (Zr−O 202.8−207.4 pm), the second bridging oxygen atom [O(2)] is slightly distorted towards a μ_2-coordination mode, with the shorter Zr−O distances [203.0(3) and 205.7(3) pm] to the metal atoms of the elongated Zr(2)−Zr(4) edge, and a longer Zr(1)−O(2) distance [217.3(3) pm].

In contrast to the edge-sharing linkage of the square antiprisms in **1**, the coordination polyhedra in **2** share either edges or vertices (Figure 6). A common edge is shared by the square antiprisms of Zr(1) and Zr(3) [μ_3-oxygen O(2) and the bridging carboxylate oxygen atom O(71)] and of Zr(1) and Zr(4) [μ_3-oxyen atoms O(1) and O(2)]. Owing to the different linkage of the polyhedra, the Zr−Zr distances in **2** (358.92−374.5 pm) are distinctly longer than in **1** [348.0(2) and 350.6(4) pm].

The Zr−O distances of the chelating OMc groups range from 220.1 to 233.0 pm. The shorter distances belong to chelating carboxylate groups *trans* to a μ-oxygen atom. The Zr−O distances of the bridging OMc ligands in **2** are significantly longer (213.5−224.8 pm) than those in **1** (210−219 pm). This is attributable to an adjustment of the bridging ligands to the larger Zr−Zr distance[10].

Figure 6. The linking of the coordination polyhedra in $Zr_4O_2(OMc)_{12}$ (**2**)



Discussion

Molecular precursors $E(OR)_{n-x}(OMc)_x$, prepared by reaction of methacrylic acid (McOH) with metal alkoxides $E(OR)_n$, are often used for the preparation of inorganic-organic hybrid polymers by sol-gel processing followed by polymerization of the organic groups. The structural organization of the building blocks from which the polymers are composed determines the properties of such materials.

Reaction of $Zr(OPr)_4$ with a 4-fold excess of methacrylic acid results in the oxo cluster $Zr_6(OH)_4O_4(OMc)_{12}$ (**1**) with two OMc ligands per zirconium atom. With a higher excess of methacrylic acid, the Zr/OMc ratio can even be increased to 3, and the cluster $Zr_4O_2(OMc)_{12}$ (**2**) is isolated. The two clusters are formally derived from $Zr(OPr)_2(OMc)_2$ and $Zr(OPr)(OMc)_3$, although we currently have no information on the sequence of the substitution and hydrolysis reactions necessary to convert $Zr(OPr)_4$ to **1** and **2**. The water responsible for hydrolysis of the alkoxy groups is generated in situ by esterification of methacrylic acid with propanol. The reaction of $Zr(OnPr)_4$ contrasts that of $Ti(OR)_4$, where the maximum degree of alkoxide substitution by carboxylate ligands is 1.33.

In comparing the structures of the carboxylate-substituted oxotitanium clusters with **1** and **2**, one has to keep in mind that a carboxylate ligand provides twice the number of oxygen atoms for coordination than a terminal alkoxide group, although both groups carry one negative charge. Thus, in $Ti_6(\mu_2\text{-}O)_2(\mu_3\text{-}O)_2(OEt)_6(\mu_2\text{-}OEt)_2(OMc)_8$ [= $Ti_6O_4(OEt)_8(OMc)_8$][6] the OEt and OMc ligands provide 2.67 negative charges and 4.33 oxygen atoms for coordination per metal atom. In **1** (**2**), the OMc ligands provide 2 (3) negative charges and 4 (6) oxygen atoms per Zr atom, i.e. the average number of coordinating atoms per negative charge is much higher. The high number of oxygen atoms available for coordination can only be accommodated by increasing the coordination number of the metal atom. While the titanium atoms in the oxo carboxylate clusters are only 6-coordinate, the zirconium atoms in **1** and **2** are, with one exception, 8-coordinate. It is thus the greater aptitude of zirconium to expand its coordination sphere which explains why more alkoxide groups can be substituted by OMc groups in $Zr(OPr)_4$ compared to $Ti(OR)_4$. Therefore, materials prepared from $Zr(OR)_4$/methacrylic acid mixtures allow a higher organic cross-linking density than materials analogously prepared from $Ti(OR)_4$.

The main structural difference between the clusters **1** and **2** is the linkage of the coordination polyhedra. The more open (less condensed) structure of **2** (partial vertex-sharing linkage instead of edge-sharing) is again a consequence of the higher degree of substitution by OMc groups. The OMc ligands in **2** already occupy six coordination sites per metal atom, and therefore only one edge or two vertices are left for condensation of the square antiprisms. The complicated manner in which this condensation is structurally realized is somewhat surprising.

There are only bridging OMc ligands in $Ti_6O_4(OEt)_8(OMc)_8$. As a consequence of the higher coordination number, which decreases the O−Zr−O angle between neighbouring coordination sites, some of the OMc ligands in **1** and **2** are also chelating.

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Experimental Section

Preparation of **1**: 1 ml of a 70% solution of $Zr(OnPr)_4$ (3.1 mmol) in *n*-propanol (Aldrich, used as received) was mixed in a Schlenk tube under Ar with 1 ml (11.8 mmol) of methacrylic acid. The closed vessel was stored at room temperature. Cluster **1** crystallized quantitatively from the solution after 1 d (yield 0.91 g, colourless crystals).

Preparation of **2**: 2 ml of a 70% solution of $Zr(OnPr)_4$ (6.2 mmol) in *n*-propanol (Aldrich, used as received) was mixed in a Schlenk tube under Ar with 8 ml (94.3 mmol) of methacrylic acid. The closed vessel was stored at room temperature. Cluster **2** crystallized quantitatively from the solution after 7 d (yield 1.90 g, colourless crystals).

X-ray Structure Analyses: **1**: Colourless crystals (0.5 × 0.4 × 0.4 mm). **2**: Colourless crystals (0.4 × 0.3 × 0.3 mm). − Cell parameters: **1**: Hexagonal, a = 1740.0(3), c = 1820.0(4) pm, V = 4772(1) × 10^6 pm^3, space group $P6_3mc$ (Z = 6), $d_{calcd.}$ = 1.16 g/cm^3 (without the intercalated solvent molecules). **2**: Monoclinic, a = 1710.11(2), b = 1736.72(1), c = 1977.88(1) pm, β = 90.086(1)°, V = 5874.3(1) × 10^6 pm^3, space group $P2_1/c$ (Z = 4), $d_{calcd.}$ = 1.60 g/cm^3. − Data collection: The crystals were mounted on a Siemens SMART diffractometer (area detector) in a sealed capillary. Mo-K_α radiation (λ = 71.073 pm, graphite monochromator) was used for all measurements. The cell dimensions were refined with all unique reflections. The data collection at 203 K covered a hemisphere of the reciprocal space, by a combination of three sets of exposures. Each set had a different ϕ angle for the crystal, and each exposure took 20 s and covered 0.3° in ω. The collected data range was $3.8° \leqslant 2\Theta \leqslant 23°$ ($-19 \leqslant h \leqslant 5$, $-16 \leqslant k \leqslant 16$, $-20 \leqslant l \leqslant 19$) for **1**, and $1.6° \leqslant 2\Theta \leqslant 23°$ ($-13 \leqslant h \leqslant 19$, $-19 \leqslant k \leqslant 19$, $-18 \leqslant l \leqslant 21$) for **2**. The crystal-to-detector distance was 3.85 cm. 10243 (**1**) and 22285 (**2**) reflections were collected, and 2444 (**1**) and 8372 (**2**) unique reflections [$R_{int.}$ = 0.081 (**1**) and 0.079 (**2**)] were obtained after correction for polarization and Lorentz effects (**1**: μ = 6.89 cm^{-1}, **2**: μ = 7.70 cm^{-1}). − Solution of the structures: The structures were solved by direct methods (SHELXS86). In the case of **2**, the positions of the hydrogen atoms were calculated according to an idealized geometry. Refinement was performed by the full-matrix least-squares method based on F^2 (SHELXL93) with anisotropic thermal parameters for all nonhydrogen atoms. The parameters of the hydrogen atoms were refined with a riding model. **1**: $R = 0.105$, $R_w = 0.281$ for 2061 refelctions with $I = 2.0\ \sigma(I)$; $w = 1/[\sigma^2(F_o^2) + (0.1429P)^2 + 31.91\ P\ [P = (F_o^2 + 2\ F_c^2)/3]$; **2**: $R = 0.036$, $R_w = 0.080$ for 7041 reflections with $I = 2.0\ \sigma(I)$; $w = 1/[\sigma^2(F_o^2) + (0.0181\ P)^2 + 13.15\ P\ [P = (F_o^2 + 2\ F_c^2)/3]$. The largest residual electron density was 1.51 (**1**) and 0.54 e/Å^3 (**2**)[11].

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[11] Further details of the crystal-structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-405990 (**1**) and -405991 (**2**).

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